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(71) Applicant: KONISHIROKU PHOTO INDUSTRY CO. LTD.  
No. 26-2, Nishishinjuku 1-chome Shinjuku-ku  
Tokyo(JP)

(72) Inventor: Hirabayashi, Shigeto  
108-17-502 Yokokawa-cho  
Hachioji-shi Tokyo(JP)

(72) Inventor: Masukawa, Toyooki  
2196-505 Hirai Hinode-machi  
Nishitama-gun Tokyo(JP)

(72) Inventor: Ishikawa, Wataru  
1214-1 Kunugida-machi  
Hachioji-shi Tokyo(JP)

(74) Representative: Ellis-Jones, Patrick George  
Armine et al,  
J.A. KEMP & CO. 14 South Square Gray's Inn  
London WC1R 5EU(GB)

(64) A method of forming an image by means of heat development.

(67) A method of forming an image is disclosed which comprises imagewise exposing a photosensitive material comprising a support having thereon a heat development photosensitive layer comprising

- (a) an organic acid silver salt;
- (b) a photosensitive silver halide;
- (c) a reducing agent; and
- (d) gelatin and/or a gelatin derivative binder,

and thereafter bringing a non-water-permeable layer into close contact with said heat development photosensitive layer so as to heat develop said layer.

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A METHOD OF FORMING AN IMAGE BY MEANS OF  
HEAT DEVELOPMENT

The present invention relates to an image forming process in which a heat development type photosensitive material is used, and more particularly to an image forming process using a heat development type photosensitive  
5 material which possesses both good sensitivity and maximum density and also fogs less.

Conventional photographic processes using a silver halide are superior to other photographic processes especially as regards photosensitiveness, gradation, image  
10 preservability and the like, and have been the ones most frequently put to practical use.

In such processes, however, a series of wet process steps such as development and fixing with processing solutions and washing with water are used so that there are  
15 many problems since it takes time and labor to process; the phytotoxicity affects the human body during the handling of the chemicals and further the processing room, and the operator's body and clothing are contaminated, and still further that environmental pollution is caused when  
20 the processing solution is discharged. There is thus a demand for photographic processes using a silver halide, which develop a photosensitive material and provide an image forming process, in the dry without using any processing solution while keeping the processed image  
25 stable under an ordinary room lamp.

There have been a great number of proposals relating to such photographic dry processes; in particular, a heat development type photosensitive material capable of being developed by a heat treatment has become the object

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of public attention as a photosensitive material which would meet these needs. Heat development type photosensitive materials which have been disclosed include a photosensitive material comprising an organic acid  
5 silver salt, a silver halide and a reducing agent as described in, for example, Japanese Patent Examined Publications Nos (hereinafter referred to as JPEP No) 4921/1968 and 4924/1968.

As for the development apparatus for the  
10 development of such a heat development type photosensitive material, a process holding the material against a heat block for a certain period of time, a process whereby the material travels along a heat block, a process using a heat drum, a process involving blowing a blast of hot air as  
15 well as a development process using infra-red rays, an electric current or a micro-wave, are known as described in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O P I Publication) Nos 158230/1979, 158231/1979, 2281/1980,  
20 1939/1981 and 4904/1981, and Research Disclosure vol 16810 and 17623.

In the known image forming processes using a heat development type photosensitive material, however, it is not always possible to obtain satisfactory photosensitivity  
25 and maximum density of the image; problems still remain such that they cannot be put to practical use.

Accordingly, it is an object of the invention to provide an image forming process using a heat development type photosensitive material with high  
30 sensitivity and sufficient maximum density, providing an excellent image with little fogging.

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According to the present invention, there is provided a method of forming an image by means of heat development of a heat development type photosensitive material comprising a support having thereon a heat development photosensitive layer containing:

- (a) an organic acid silver salt;
- (b) a photosensitive silver halide;
- (c) a reducing agent; and
- (d) gelatin and/or a gelatin derivative binder,

comprising the steps of imagewise exposing said layer and thereafter of bringing a non-water-permeable layer into close contact with said heat development photosensitive layer to make a heat development.

When such a heat development type photosensitive material is exposed imagewise and then brought into close contact with a non-water-permeable layer so as to prevent moisture from evaporating from the photosensitive layer of said photosensitive material and heat development is carried out in this way, it is found that the development of a heat development type photosensitive material in which gelatin and/or a derivative thereof serve as binder is remarkably accelerated, and the photographic characteristics thereof are also improved. These results are most surprising. The reason why development is accelerated is not completely clear; however, it may be because the moisture is prevented from leaving the gelatin being heat-developed, by the non-water-permeable layer in close contact with the surface of the photosensitive layer, and because the gelatin is softened by the moisture at the heat-development temperature giving it characteristics similar to that of a thermoplastic binder so that the development is accelerated remarkably.

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As for the amount of water necessary to give the gelatin such characteristics, it is generally sufficient to have an equilibrium moisture content between the gelatin and said photosensitive material under 20 - 100% relative humidity; sharp increases in the sensitivity and the maximum density cannot be expected until the moisture is prevented from being eliminated, for example by evaporation during heat development.

The following is a detailed description of the invention.

The image forming processes of the invention are those in which the aforesaid heat development type photosensitive material is exposed imagewise and a non-water-permeable layer is then brought into close contact with the surface of the heat development type photosensitive material for heat development. Specific processes may be roughly classified into the following two:

1. A process in which a sheet of material comprising a non-water-permeable substance or a sheet of material having a non-water-permeable layer such as a resin-coated paper is laid in advance on the surface of the photosensitive layer of the heat development type photosensitive material before development is carried out and heat development is then carried out while keeping the two materials in close contact.

Specific examples of substances which can serve as the non-water-permeable layer include high molecular compounds such as polyethylene, polypropylene, polystyrene, polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl fluoride, polyvinyl pyrrolidone,

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polyvinyl chloride, ethyl polyacrylate, methyl polymethacrylate, ethyl polymethacrylate, polyvinylidene chloride, chlorinated polyethylene, chlorinated polypropylene, polycarbonate, polybutadiene, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, ethyl cellulose, benzyl cellulose, cellulose acetate phthalate, polyethylene terephthalate, or fluorine-contained polymer (e.g. polytetrafluoroethylene) or polyamide.

The non-water-permeable layer comprising said non-water-permeable substance may be peeled off after heat development is complete or it can be allowed to remain in use.

2. A process in which a non-water-permeable layer is arranged within the heat development means and the surface of the heat development type photosensitive layer is brought into close contact with said non-water-permeable layer and development is carried out while keeping the two in close contact.

The area of the heat development means remaining in contact with the surface of the heat development type photosensitive layer is made non-water-permeable; an example of said means is illustrated, merely by way of example, by the heat drum type heat development means shown in section in accompanying Figure 1, the drum surface being formed of a non-water-permeable substance.

In Figure 1, reference numeral 1 designates a heat drum with a non-water-permeable substance coated on its surface. Examples of suitable non-water-permeable substances include a single substance, for example, a metal such as iron, nickel, chromium, copper, aluminium or titanium or an alloy thereof, glass, polystyrene, polyethylene, polycarbonate or polyethylene terephthalate;

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2 is a rotary shaft; 3 is a belt tensioned to come into pressure contact with the surface of the heat drum; 4 is a support roller for tensioning said belt 3; 5 is a heat development type photosensitive material; 6 is a reel for supplying said photosensitive material 5; 7 is a reel for taking up said photosensitive material 5; and 8 is a motor for revolving said heat drum 1.

In operation, in the developing means, an exposed heat development type photosensitive material 5 is conveyed from supply reel 6 along belt 3 in the direction of the arrow and is then heat-developed while keeping the non-water-permeable layer formed on the surface of heat drum 1 in contact with the surface of the photosensitive layer; in this way, the photosensitive material 5 is developed completely and taken up by the take-up reel 7.

Figure 2 illustrates another example of a development means which can be used in the present invention, bringing non-water-permeable layers into close contact at the same time with both surfaces of the heat development type photosensitive material.

In Figure 2, the reference numerals have the same significance as those in Figure 1. Reference 10 is a cover comprising a non-water-permeable substance which is so arranged as to cover the face of the belt 3 opposite the side facing the heat drum 1.

In using the development means, when heat development type photosensitive material 5 is developed by means of heat drum 1, the surface of the photosensitive drum is coated with a non-water-permeable layer formed on the surface of heat drum 1 and at the same time the rear face of material 5 is covered by cover 10 of non-water-permeable substance suspended in tension by belt 3 so as to prevent moisture from escaping; therefore, the use of

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this development means is particularly effective for accelerating development.

Examples of organic acid silver salts which can be used in the heat development type photosensitive material are given, as described in JPEP Nos 4921/1968, 26582/1969, 18416/1970, 12700/1970 and 22185/1970; Japanese Patent O P I Publication Nos 52626/1974, 31728/1977, 137321/1977, 141222/1977, 36224/1978 and 37610/1978; and US Patent Nos 3 330 633, 3 794 496, 4 105 451, 4 123 274 and 4 168 980; a silver salt of an aliphatic carboxylic acid such as silver laurate, silver myristate, silver palmitate, silver stearate, silver arachidonate, silver behenate, silver- $\alpha$ -(1-phenyl-tetrazole thio)acetate; a silver salt of an aromatic carboxylic acid such as silver benzoate or silver phthalate; a silver salt of an organic compound having an imino group such as a silver salt of benzotriazole, saccharin, phthalodion, or phthalimide; a silver salt of a compound having a mercapto or thione group such as a silver salt of mercaptobenzoxazole, mercaptotriazole, 2-mercaptobenzothiazole, 2-mercaptobenzoimidazole or 3-mercapto-4-phenyl-1,2,4-triazole; as well as the silver salt of 4-hydroxy-6-methyl-1,3,3a,7-tetra-zaindene or 5-methyl-7-hydroxy-1,2,3,4,6-benzozaindene.

Of these organic acid silver salts, a silver salt of an aliphatic carboxylic acid is preferred, a silver salt of a long chain aliphatic carboxylic acid having 18 - 33 carbon atoms being particularly preferred.

In the image forming process of the invention, examples of silver halides which can be used include silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chloroiodide, silver iodobromide and silver chloroiodidobromide. Said photosensitive



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silver halide can be prepared in any desired manner such as by a single-jet process or a double-jet process which are known in the photographic field; in particular, a preferred effect can be attained by making use of a gelatin-  
5 silver halide emulsion prepared by one of the methods or techniques for preparing a gelatin-silver halide photographic emulsion.

The photosensitive silver halide may also be chemically sensitized in any known manner. Suitable  
10 sensitization processes include gold sensitization, sulfur sensitization, a gold-sulfur sensitization, or a reduction sensitization.

The photosensitive silver halide may be coarse-grained or fine-grained; preferable grain sizes  
15 for the longitudinal dimension are approximately 1.5 to 0.001 microns, especially approximately 0.5 to 0.05 microns.

A photosensitive silver halide emulsion thus prepared may be applied as a layer of said photosensitive  
20 material.

Other processes for preparing a photosensitive silver halide include one where a photosensitive silver halide is formed in a portion of an organic acid silver salt by making a component for forming a photosensitive  
25 silver salt co-exist therewith. Components for forming a photosensitive silver salt which can be used in such a process include an inorganic halogenide of formula  $MX_n$ , wherein M represents an H atom,  $NH_4$  group or a metallic atom group; X represents a Cl, Br or I atom; n is one  
30 when M represents an H atom or  $NH_4$  group, or corresponds to the valency of the metallic atom when M represents said metallic atom. Suitable metallic atoms include

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lithium, sodium, potassium, rubidium, caesium, copper, gold, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminium, indium, lanthanum, ruthenium, thallium, germanium, tin, lead, antimony,

5 bismuth, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, rhodium, palladium, osmium, irridium, platinum and cerium; a halogen-containing metallic complex such as  $K_2PtCl_6$ ,  $K_2PtBr_6$ ,  $HAuCl_4$ ,  $(NH_4)_2IrCl_6$ ,  $(NH_4)_3IrCl_6$ ,  $(NH_4)_2RuCl_6$ ,  $(NH_4)_3RuCl_6$ ,  $(NH_4)_3RhCl_6$

10 or  $(NH_4)_3RhBr_6$ ; an onium halide, for example a quaternary ammonium halide such as tetramethyl ammonium bromide, trimethylphenyl ammonium bromide, cetyl ethyl dimethyl ammonium bromide, 3-methyl thiazolium bromide and trimethyl benzyl ammonium bromide, a quaternary phosphonium

15 halide such as tetraethyl phosphonium bromide, a tertiary sulfonium halide such as benzyl ethyl methyl bromide and 1-ethyl thiazolium bromide; a halogenated hydrocarbon such as iodoform, bromoform, carbon tetrabromide and 2-bromo-2-methyl propane; an N-halogenide such as

20 N-chlorosuccinimide, N-bromosuccinimide, N-bromophthalimide, N-bromoacetamide, N-iodosuccinimide, N-bromophthaladinone, N-chlorophthaladinone, N-bromacetanilide, N,N-dibromo-benzene sulfonamide, N-bromo-N-methyl benzene sulfonamide and 1,3-dibromo-4,4-dimethyl hydantoin; and other

25 halogenides such as triphenyl methyl chloride, triphenyl methyl bromide-2-bromobutyric acid and 2-bromethanol.

Said photosensitive silver halide and said components for forming a photosensitive silver salt may be used together in a variety of processes; suitably

30 0.001 to 1.0 mol, preferably 0.01 to 0.3 mol, per mol of organic acid silver salt is used.

In the image forming processes of the invention, typical reducing agents which can be used in the heat development type photosensitive material include a phenol such as p-phenylphenol, p-methoxy phenol, 2,6-di-tert-butyl-p-cresol and N-methyl-p-aminophenol; a sulfonamido phenol such as 4-benzene sulfonamido phenol, 2-benzensulfonamido phenol, 2,6-dichloro-4-benzenesulfonamido phenol and 2,6-dibromo-4-(p-toluene sulfonamido)phenol; a di- or polyhydroxy benzene such as hydroquinone, tert-butyl hydroquinone, 2,6-dimethyl hydroquinone, chlorohydroquinone, carboxy hydroquinone, catechol and 3-carboxy catechol; a naphthol such as  $\alpha$ -naphthol,  $\beta$ -naphthol, 4-aminonaphthol and 4-methoxynaphthol; a hydroxy binaphthyl and a methylene bisnaphthol such as 1,1'-dihydroxy-2,2'-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, 6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl, 4,4'-dimethoxy-1,1'-dihydroxy-2,2'-binaphthyl and bis(2-hydroxy-1-naphthyl)methane; a methylene bisphenol such as 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethyl hexane, 1,1-bis(2-hydroxy-3-tert-butyl-5-methyl phenyl)methane, 1,1-bis(2-hydroxy-3,5-di-tert-butyl phenyl)methane, 2,6-methylene bis(2-hydroxy-3-tert-butyl-5-methyl phenyl)-4-methyl phenol,  $\alpha$ -phenyl- $\alpha,\alpha$ -bis(2-hydroxy-3,5-di-tert-butyl phenyl)methane,  $\alpha$ -phenyl- $\alpha,\alpha$ -bis(2-hydroxy-3-tert-butyl-5-methyl phenyl)methane, 1,1-bis(2-hydroxy-3,5-dimethyl phenyl)-2-methyl propane, 1,1,5,5-tetrakis(2-hydroxy-3,5-dimethyl phenyl)-2,4-ethyl pentane, 2,2-bis(4-hydroxy-3,5-dimethyl phenyl)propane, 2,2-bis(4-hydroxy-3-methyl-5-tert-butyl phenyl)propane and 2,2-bis(4-hydroxy-3,5-di-tert-butyl phenyl)propane; ascorbic acid; a 3-pyrazolidone, a pyrazoline; a pyrazolone; a hydrazone; and a paraphenylene diamine.

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When a hydrazine and paraphenylenediamine are used as reducing agent, a color image can be obtained in combination with a phenol or naphthol compound and a compound having an activated methylene such as pyrazolone, pyrazolotriazole, indazole, pyrazolobenzimidazole and pyrazoline, as described in US Patents Nos 3 531 286 and 3 764 328, and Japanese Patent O P I Publication No 27132/1981. The aforesaid reducing agents may be used singly or in combination. The amount used depends upon the nature of the organic acid silver salts, for example, and other additives such as a color toning agent, but it is normally 0.05 - 10 mol, preferably 0.1 - 3 mol, per mol of organic acid silver salt.

In the invention, the binders used in the heat development type photosensitive material comprise substantially gelatin and/or derivatives thereof. It is preferable that said binders are composed of gelatin and/or derivatives thereof; in addition it will generally not be disadvantageous for the material to contain a water-soluble binder other than gelatin and/or a derivative thereof such as polyvinyl alcohol, polyacrylamide or carboxymethyl cellulose provided that such a binder does not interfere with the desired effects of the invention.

Examples of the binders for a heat development type photosensitive material in which gelatin is used have been described in US Patent No 4 168 980, and Japanese Patent O P I Publication Nos 52626/1974 and 116144/1978, and JPEP Nos 26582/1969, 12700/1970 and 18416/1970. In a heat development type photosensitive material in which gelatin serves as the binder, it is possible to use a highly sensitive gelatin-silver halide emulsion in which the sensitivity of the photosensitive silver halide has been increased in a variety of ways; therefore extremely high sensitivity can be obtained as compared with the case when using other types of non-water-soluble binder. It is also

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possible to prevent said photosensitive material from blackening caused by "printing-out" of an unexposed area after processing, because unexposed silver halide can be removed in a fixing step with an ordinary type of  
5 fixing solution after heat development. When using a color photosensitive material, bleaching and bleach-fixing can easily be carried out; further, as compared with the case of using a thermoplastic binder, because gelatin is not a thermoplastic binder, there is no  
10 binder softening that accelerates the development at the heat development temperature.

According to the aforesaid process of the invention, the merits of using gelatin and/or a derivative thereof (i.e. the maximum density and the sensitivity  
15 thereof are high) as binder are in no way masked.

When gelatin and/or a derivative thereof is used as binder and the aforesaid organic acid silver salt is dispersed therein, water can be used as the solvent; it is preferred to use water of 50% or less by weight  
20 in combination with a miscible organic solvent in order to improve the dispersability.

Suitable organic solvents for this purpose include a lower alcohol such as methanol, ethanol, isopropanol and n-propanol; acetone; methyl ethyl ketone,  
25 ethylene glycol, propylene glycol, glycerol, ethylene glycolmonomethyl ether, ethylene glycol monoethyl ether and dioxane.

A surface active agent is also effective for improving the dispersibility. The surface active agent  
30 may be anionic, cationic, amphoteric or non-ionic,

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especially the anionic surface active agents such as alkylbenzene sulfonate and alkylnaphthalene sulfonate. The amount thereof used is suitably 0.01% to 10.0%, more preferably 0.1% to 5.0%, by weight relative to the amount  
5 of organic acid silver salt.

A color toning agent can be included in the heat development type photosensitive material for the purpose of blackening the image.

Suitable color toning agents include phthalimide,  
10 pyrazolone, quinazolinone, N-hydroxy naphthalimide, benzoxazine, naphthoxazine, 2,3-dihydro-phthalazinedione, 2,3-dihydro-1,3-oxazine-2,4-dione, oxypyridine, aminopyridine, hydroxyquinoline, aminoquinoline, isocarbostyryl, sulfonamide, 2H-1,3-benzothiazine-2,4-(3H)-dione,  
15 benzotriazine, mercaptotriazole, dimercaptotetrazapentalene, phthalic acid, naphthalic acid, aminophthalic acid, or phthalazinone, and derivatives thereof, as described in Japanese Patent O P I Publications Nos 4928/1971, 6077/1971, 5019/1974, 5020/1974, 91215/1974, 107727/1974,  
20 2524/1975, 67132/1975, 67641/1975, 114217/1975, 33722/1977, 99813/1977, 1020/1978, 55115/1978, 76020/1978, 125014/1978, 156523/1979, 156524/1979, 156525/1979, 156526/1979, 4060/1980, 4061/1980 and 32015/1980; West German Patents Nos 2 140 416, 2 147 063 and 2 220 618; and US Patents Nos 3 080 254,  
25 3 847 612, 3 782 941, 3 994 732, 4 123 282 and 4 201 582.

An anti-foggant may also be included in the heat development type photosensitive material of the invention.

Suitable anti-foggants include a mercuric salt;  
30 an oxidation agent such as an N-halogenacetamide, an N-halogenosuccinimide, perchloric acid or a salt thereof, an inorganic peroxide and a persulfate; an acid or a

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salt thereof such as sulfonic acid, lithium laurate, rosin, diterpenic acid and thiosulfinic acid; a sulfur containing compound such as a mercaptol-releasable compound, thiouracil, disulfide, sulfur, mercapto-1,2,4-triazole, 5 thiazolinethione and a polysulfide compound; also an oxazoline or a compound such as 1,2,4-triazole or phthalimide; as stated in JPEP No 11113/1972; Japanese Patent O P I Nos 90118/1974, 10724/1974, 97613/1974, 101019/1975, 130720/1974, 123331/1975, 10 47419/1976, 57435/1976, 78227/1976, 104338/1976, 19825/1978, 20923/1978, 50725/1976, 3223/1976, 42529/1976, 81124/1976, 51821/1979 and 93149/1980; British Patent No 1 455 271; US Patents Nos 3 885 968, 3 700 457, 4 137 079 and 4 138 265; and West German Patent No 15 2 617 907.

The heat development type photosensitive material of the invention can also contain a variety of known additives as required such as a water-holding compound, a spectral sensitization dye, an anti-halation 20 dye, a print-out preventive or a non-mercuric anti-foggant.

Suitable water-holding compounds include hydroxyethyl cellulose, carboxymethyl cellulose, polyalkylene oxide (i.e. polyglycol) or an organic acid.

25 Spectral sensitization dyes which can be used include those which are effective for a silver halide emulsion, for example cyanine, merocyanine, rhodacyanine and styryl dyes.

Suitable print-out preventives include tetra- 30 bromobutane, tribromoethanol, 2-bromo-2-tolylacetamide, 2-bromo-2-trisulfonylacetamide, 2-tribromomethyl sulfonyl benzothiazole and 2,4-bis(tribromomethyl)-6-methyl triazine.

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As supports which can be used in the heat development type photosensitive materials of the invention, there may be mentioned synthetic plastic-films such as polyethylene film, a cellulose acetate film and a poly-  
5 ethylene terephthalate film and sheet of paper such as a master paper for photographic use, a printing paper, a baryta paper or a resin coated paper.

The above-mentioned composites are coated over said support with a binder and a suitable solvent.  
10 The thickness of the coating is suitably 1 to 1 000  $\mu$ , and more preferably 3 to 20  $\mu$ , thick after drying.

It is also possible to include a superposing layer on the heat development type photosensitive layer as occasion demands.

15 A heat development type photosensitive material thus prepared is imagewise exposed and then developed only by heating for, say, 1 to 60 seconds, typically at a temperature of 80° to 200°C.

A preliminary heating at a temperature of, say,  
20 70° to 180°C before an exposure is made, can be carried out if necessary.

Suitable light sources for image exposure, include a tungsten lamp, a fluorescent lamp, a mercury lamp, an iodine lamp, a xenon lamp, a CRT light source and a  
25 laser beam source.



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The following Examples further illustrate the present invention.

EXAMPLE 1

A solution in which 54.4 g of behenic acid  
5 were dissolved in 1200 ml of toluene, was mixed with  
2400 ml of water and the aqueous solution thus obtained  
was homogenized by means of a high-speed homogenizer.  
Ammoniacal silver nitrate solution (400 ml) containing  
27.2 g of silver nitrate were dripped into said solution  
10 over 30 minutes, keeping the temperature of the reacting  
solution at 60°C with agitation; agitation was continued  
for another 30 minutes, and then the crystals thus  
produced were filtered, washed, cleaned with methanol  
and dried under reduced pressure; thus 65.0 g of silver  
15 behenate were obtained.

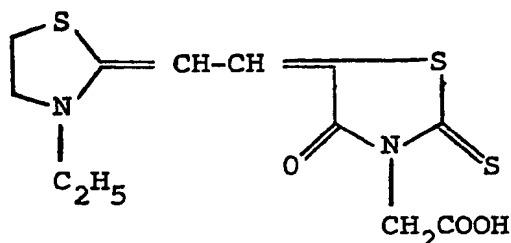
A dispersed solution was prepared by adding  
200 ml of ethanol, 100 ml of 10% aqueous gelatin solution,  
100 ml of water and 8 ml of 10% aqueous solution of  
Alkanol B (alkyl naphthalene sulfonate, manufactured  
20 by DuPont) to 9.0 g (0.02 mol, approximately) of  
the silver behenate thus obtained and the ultrasonic  
wave dispersion was applied thereto. A coating solution  
was prepared by adding the following components in order  
with agitation to said dispersion.

25 (Components)

- (1) Phthalazinone (Methanol solution 5%, by weight); 20 ml.
- (2) Mercuric acetate (Methanol solution 1%, by weight);  
10 ml.
- (3) Silver bromide Emulsion (Cubical emulsion having an  
30 average grain diameter of 0.2 microns containing 60 g  
of gelatin and 0.353 mol of silver per kg of the  
emulsion); 9 ml.

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- (4) Sensitization dye (Methanol solution 0.05%, by weight of merocyanine dye of formula below); 2.5 mol.



- (5) Hydroquinone (Methanol solution 5%, by weight); 25 ml.

- 5 A heat development type photosensitive material (A) was prepared by coating the coating solution prepared as above onto a sheet of raw paper for photographic use so that the amount of silver was 0.5 g per m<sup>2</sup>.

- The heat development type photosensitive material 10 (A) thus prepared was exposed imagewise to white light through a step-wedge. The exposure amounted to 1600 CMS (i.e. candela.meter.second).

- Next, Sample-1 was prepared as follows:  
a polyethylene terephthalate sheet, 50  $\mu$  thick was  
15 superposed on the surface of the heat development type photosensitive layer of the exposed heat development type photosensitive material (A) and heat was applied at 110°C for ten seconds, for development. As a control, Sample-2 was prepared by heating the exposed heat development type  
20 photosensitive material (A) as it was at 110°C for ten seconds for development. The results observed therefrom are indicated in Table 1.

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TABLE 1

	Maximum Density	Minimum Density	Relative Sensitivity
5 Sample-1 (The invention)	1.65	0.20	840
Sample-2 (Control)	0.65	0.15	100

In the table, the relative sensitivity is given relative to the sensitivity of Sample-2, taken as 100.

10 From these results, it can be seen that the sample prepared by the image forming process of the invention possesses excellent maximum density and also sensitivity as compared with that of the control sample.

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EXAMPLE 2

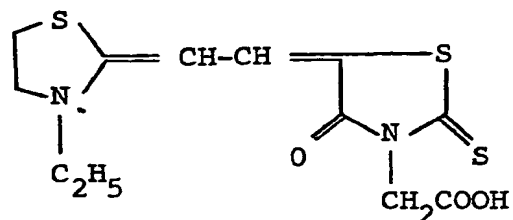
Silver salt of benzotriazole (11.9 g) was dissolved in 100 ml of methanol and the solution thus obtained was dripped into a solution of 16.9 g of silver  
5 nitrate dissolved in 200 ml of water, over five minutes.

The crystals thus produced were filtered, washed and further washed with methanol, and then dried under reduced pressure; 21.0 g of silver salt of benzotriazole were obtained. 4.5 g (0.02 mol, approximately)  
10 of this silver salt were mixed with 100 ml of 10% gelatin solution, 100 ml of water, and 4 mol of 10% aqueous solution of Alkanol B (i.e. alkyl naphthalene sulfonate, manufactured by DuPont) and a dispersed solution was obtained using an ultrasonic-wave dispersion process.

15 A coating solution was then prepared by adding the following components in succession with agitation.

## (Components)

- (1) Phthalazinone (Methanol solution 5%, by weight); 20 ml.
- (2) Mercuric acetate (Methanol solution 1%, by weight);  
20 5 ml.
- (3) Silver bromide (Cubical emulsion having an average grain diameter of 0.2 microns containing 60 g of gelatin and 0.353 mol of silver per kg of the emulsion); 9 ml.
- 25 (4) Sensitization dye (Methanol solution 0.05%, by weight, of merocyanine dye of formula below); 2.5 ml.



(5) Hydroquinone (Methanol solution 5%, by weight); 25 ml.

A heat development type photosensitive material (B) was prepared by coating the coating solution prepared as above onto a sheet of raw paper for photographic use so that the amount of silver was 0.6 g per m<sup>2</sup>.

The heat development type photosensitive material (B) thus prepared was exposed imagewise to white light through a step-wedge. The exposure amounted to 1600 CMS (i.e. candela.meter.second).

Next, Sample-3 was prepared as follows:  
a triacetyl cellulose sheet 50  $\mu$  thick was superposed on the surface of the heat development type photosensitive layer of exposed heat development type photosensitive material (B) and heat was applied at 120°C for ten seconds for development. As a control, Sample-4 was prepared by heating the exposed heat development type photosensitive material (B) as it was at 120°C for ten seconds for development. The results observed therefrom are indicated in Table 2.

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TABLE 2

	Maximum Density	Minimum Density	Relative Sensitivity
5 Sample-3 (The invention)	1.08	0.10	340
Sample-4) (Control)	0.42	0.09	100

In the table, the relative sensitivity is given relative to the sensitivity of Sample-4, taken as 100.

10 From the results, it can be seen that the sample prepared by an image-forming process of the invention possesses excellent maximum density and sensitivity as compared with that of the control sample.

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EXAMPLE 3

The heat development type photosensitive materials (A) and (B) were exposed imagewise to white light through step-wedges. In each case the exposure amounted to 5 1600 CMS (i.e. candela.meter.second). Next, the surface of the heat development type photosensitive layer of the photosensitive material (A) was heated at 110°C and that of the material (B) at 120°C for ten seconds by bringing them into close contact with the heat drum of a 10 heat drum type heat development apparatus of the type shown in Figure 1, for development to obtain Sample-5 and Sample-6, respectively. As for the drum coated with a non-water-permeable substance shown in Figure 1, the drum had a chrome-plated iron surface; a fabric belt was 15 used.

As a control, Sample-7 and Sample-8 were prepared in a similar manner, except that the photosensitive materials (A) and (B) were turned over so that the surface of the photosensitive layer faced away from the surface 20 of the heat drum and development was then carried out. The results obtained therefrom are shown in Tables 3 and 4.

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TABLE 3

		Maximum Density	Minimum Density	Relative Sensitivity
5	Sample-5 (The invention)	1.62	0.20	880
	Sample-7 (Control)	0.65	0.15	100

TABLE 4

10		Maximum Density	Minimum Density	Relative Sensitivity
	Sample-6 (The invention)	1.12	0.10	380
	Sample-8 (Control)	0.42	0.09	100

15           The relative sensitivity indicated in the above  
tables is the relative sensitivity taking the sensitivity  
of Sample-7 and Sample-8, respectively as 100.  
From the above results, it can be seen that the samples  
prepared in an image forming process of the invention  
20 possess excellent maximum density and sensitivity as  
compared with the control samples.



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C L A I M S

1. A method of forming an image which comprises imagewise exposing a photosensitive material comprising a support having thereon a heat development photosensitive layer comprising

- (a) an organic acid silver salt;
- (b) a photosensitive silver halide;
- (c) a reducing agent; and
- (d) gelatin and/or a gelatin derivative binder,

and thereafter bringing a non-water-permeable layer into close contact with said heat development photosensitive layer so as to heat develop said layer.

2. A method according to claim 1, wherein the heat development is performed while said layers are put in close contact.

3. A method according to claim 1, wherein the heat development is performed after the said layers have been put in close contact.

4. A method according to any one of claims 1 to 3, wherein the non-water-permeable layer comprises a high molecular compound, a metal, a metal alloy or glass.

5. A method according to claim 4, wherein the high molecular compound is polyethylene, polypropylene, polystyrene, polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl fluoride, polyvinyl pyrrolidone,

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polyvinyl chloride, polyethyl acrylate, polymethyl methacrylate, polyethyl methacrylate, polyvinylidene chloride, chlorinated polyethylene, chlorinated polypropylene, polycarbonate, polybutadiene, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, ethyl cellulose, benzyl cellulose, cellulose acetate phthalate, polyethylene terephthalate, fluorine-contained polymer and polyamide.

6. A method according to any one of claims 1 to 5, wherein the non-water-permeable layer is provided on the surface of a heat drum of the means for heat development.

7. A method according to any one of claims 1 to 6, wherein the non-water-permeable layer is brought into close contact with both surfaces of the photo-sensitive material.

FIG. 1

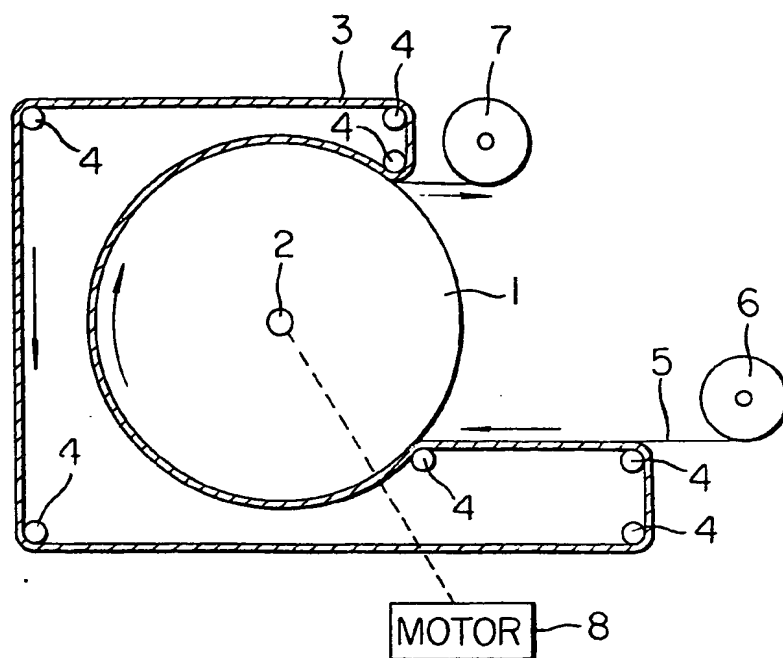
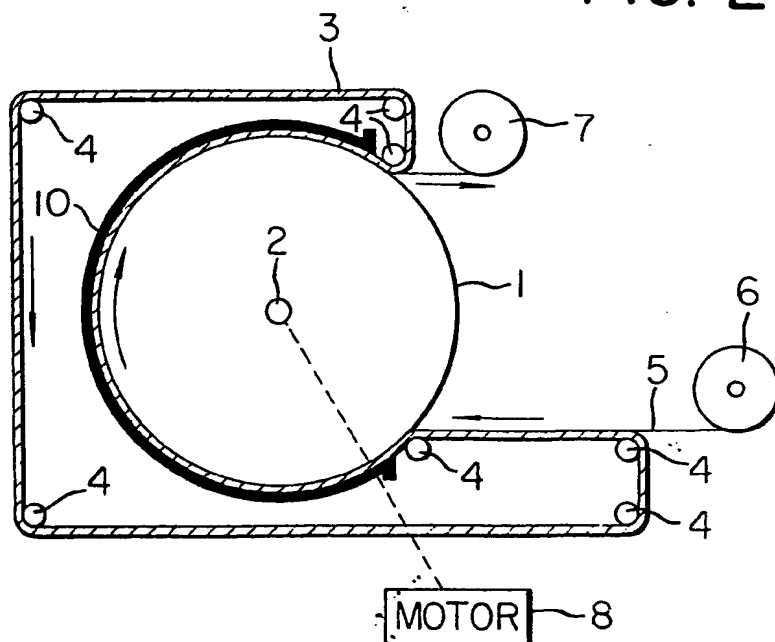


FIG. 2





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number  
**0071488**  
EP 82304047.2

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Incl. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,X	<u>US - A - 4 168 980 (ROSSA)</u> * Claims 1,2,5,6; column 1, line 1 - column 2, line 31; column 9, lines 18-32 * --	1	G 03 C 5/26 G 03 C 1/42 G 03 C 1/06
A,D	<u>US - A - 3 531 286 (RENFREW)</u> * Claims * ----	1,3-5	
			TECHNICAL FIELDS SEARCHED (Incl. Cl. 3)
			G 03 C
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search VIENNA		Date of completion of the search 08-11-1982	Examiner SCHÄFER

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